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CLEERS: Aftertreatment Modeling and Analysis

FENG GAO, JAMIE HOLLADAY, KEN RAPPE, CHAITANYA SAMPARA, MARK STEWART, JANOS SZANYI, DIANA TRAN, YILIN WANG, YONG WANG (P.I.)

PACIFIC NORTHWEST NATIONAL LABORATORY

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ACS023

Overview

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Timeline

- Status: On-going core R&D
- DPF activity originated in FY03
- Now also includes LNT (and PNA), SCR, and LTAT technologies

Budget

- FY16 funding - $770K
- FY17 funding - $770K
    - SCR task
    - Particulate/Filtration task
    - PNA task (limited)
    - LTAT activities

Barriers

- Emission controls contribute to durability, cost and fuel penalties
    - Low-temp performance is now of particular concern
- Improvements limited by:
    - Available modeling tools
    - Chemistry fundamentals
    - Knowledge of material behavior
- Effective dissemination of information

Partners

- DOE Advanced Engine Crosscut Team
- CLEERS Focus Group
- 21CTP partners
- USCAR/USDRIVE ACEC team
- Oak Ridge National Lab
- Kymanetics, Inc.
- NSF/DOE-funded program with partners at Purdue, Notre Dame, WSU, Cummins, and ANL

Relevance (and Goals)

- "CLEERS is a R&D focus project of the Diesel Cross-Cut Team. The overall objective is to promote development of improved computational tools for simulating realistic full-system performance of lean-burn engines and the associated emissions control systems."

CLEERS PNNL Subprogram Goal

Working closely with our National Lab partners, the CLEERS industrial/academic team and in coordination with our CRADA portfolio, PNNL will…

…provide the practical & scientific understanding and analytical base required to enable the development of efficient, commercially viable emissions control solutions and modeling tools for ultra high efficiency vehicles.

- VT program goals are achieved through these project objectives:
  - interact with technical community to identify relevant technological gaps
  - understand fundamental underlying mechanisms and material behavior
  - develop analytical and modeling tools, methodologies, and best practices
  - apply knowledge and tools to advance technologies leading to reducing vehicle emissions while improving efficiency
- Specific work tasks in support of the objectives are arrived at through:
  - focus group industrial monthly teleconferences, diesel cross-cut meetings
  - yearly workshops and surveys
  - ongoing discussions on program priorities with the VT office

Approach/Strategy

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Approach - "Science to Solutions"

- Build off of our strong base in fundamental sciences and academic collaborations
  - Institute for Integrated Catalysis (IIC)
  - Environmental Molecular Sciences Laboratory (EMSL)
- Orient strongly towards applications and commercialization
  - OEMs
  - TIER 1 suppliers
- Work closely with our partners and sponsors
  - ORNL (coordination of website, workshops, etc.)
  - DOE Advanced Engine Cross-Cut Team

Foundational (CLEERS)		CRADA Activities
• SCR • LTAT • PNA • Particulate/Filtration	⟷	• Standard LT SCR (FCA) • Standard LT fast SCR (Cummins/JMI) • Advanced emission controls (Cummins/JMI)) • SCR dosing system (USCAR) • Fuel neutral particulate studies (GM) • SCR-DPF (PACCAR)

Strategy – "Balanced portfolio"

- Utilize open CLEERS work to support industry CRADA activities, e.g., fundamental SCR studies led to the new CRADAs with FCA and Cummins
- Maintain clear separation between CLEERS and CRADA activities

(only CLEERS project scope covered in this presentation)

Technical Milestones and Go/No-Go Decisions

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Milestones:

Provide fundamental understanding of zeolite supported Pd PNA materials	12/31/2017	on track
Understand the mechanisms of low-temperature SCR on Cu/SSZ-13	3/30/2017	√
Elucidate the deactivation of Cu/SSZ-13 under hydrothermal aging	6/30/2017	√
Analyze X-Ray CT data and attempt to identify catalyst location in a commercial SCR-filter	3/30/2017	√
Complete PNA hydrothermal stability and sulfur tolerance studies	6/30/2018	initiated

Go/No-Go Decisions:

Demonstrate sufficient catalyst activity at 175˚C	3/30/2017	√
Identify key barriers to overcoming the "150˚C Challenge", and demonstrate a clear path to achieve sufficient catalyst activity at 150˚C	9/30/2018	on track

Technical Accomplishments (SCR task): Understanding SCR Mechanisms to Improve the Low Temperature Activity of Cu/SSZ-13 Catalysts

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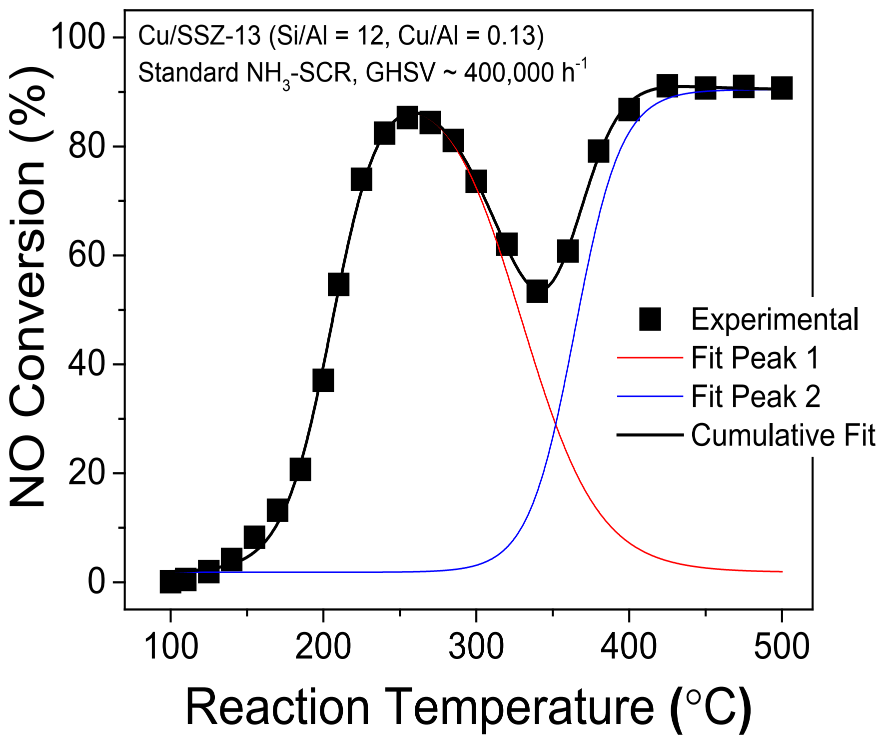
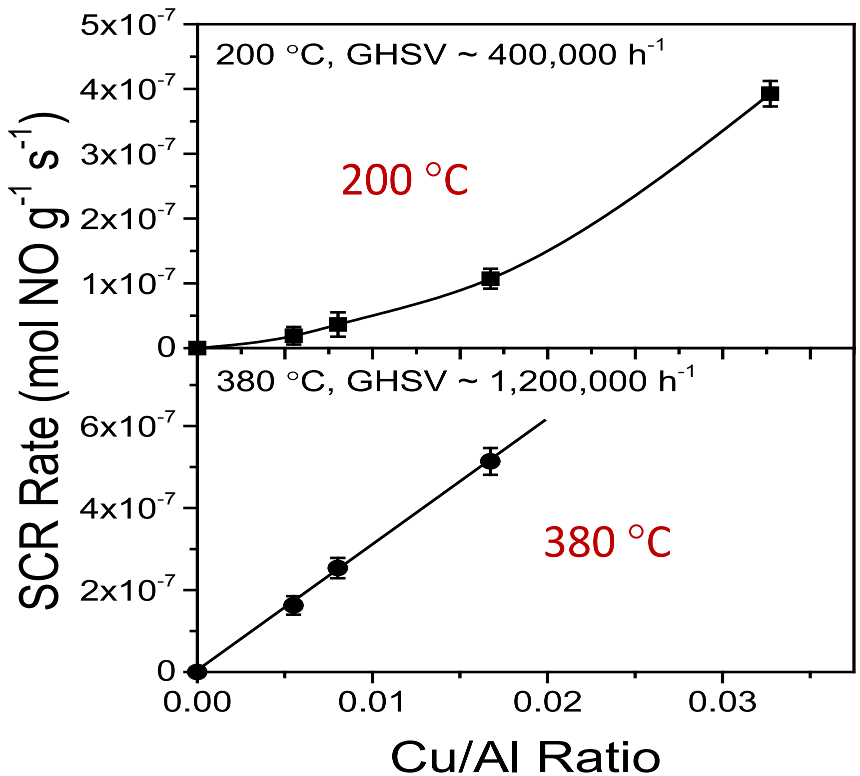
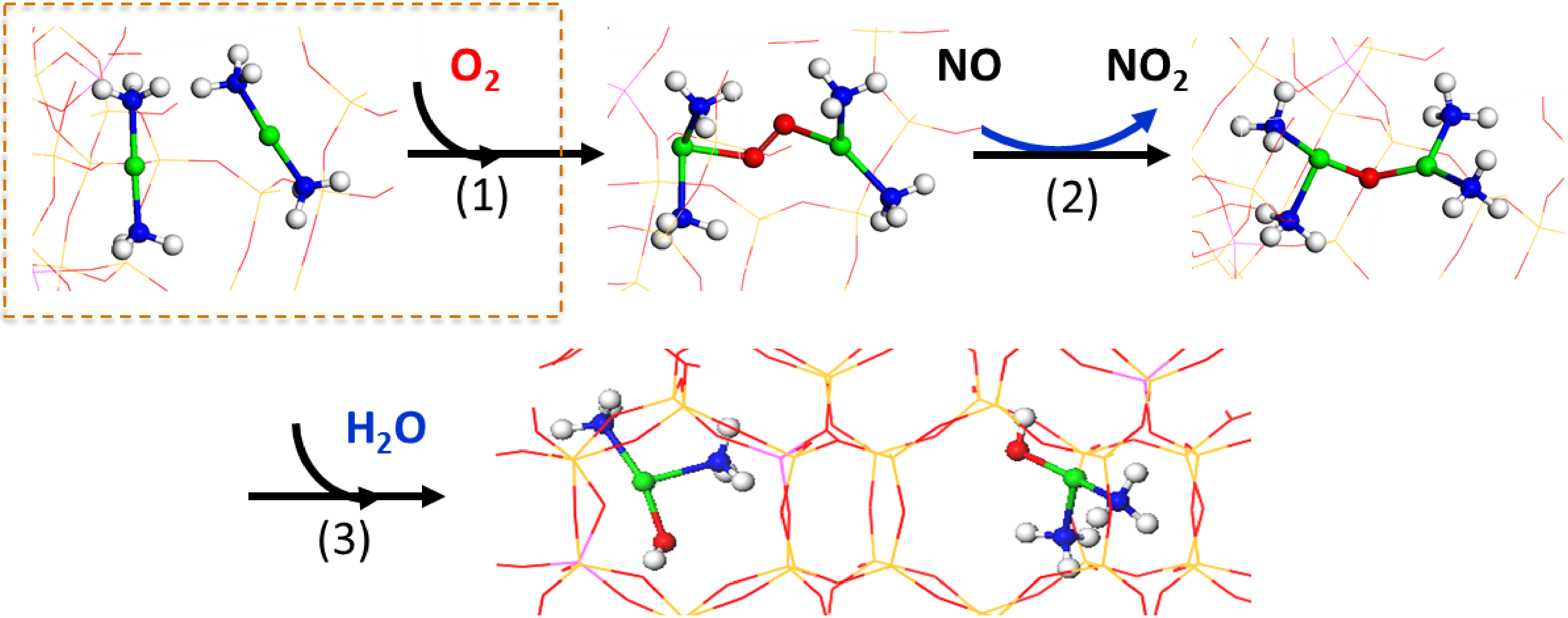




- Light-off curve for NO conversion decreases with increasing temperature between 250 and 350˚C.
- Two kinetic regimes are present:
  - SCR rate increases linearly with the square of Cu/Al ratio at 200˚C
  - SCR rate increases linearly with the Cu/Al ratio at 380˚C

Technical Accomplishments (SCR task): Developed Dual-site Mechanism for Low Temperature SCR on Cu/SSZ-13 Catalysts



Feng *et al*, *J.Am.Chem.Soc.*, 2017, 139, 4935-4942.

- The rate limiting step of Cu(I) oxidation involves the two isolated Cu(I) ions to form a transient intermediate.
- Low temperature SCR activity of Cu/SSZ-13 can be improved by maximizing the Cu loading without negatively impacting NH_3 selectivity and catalyst stability.
- New insight is provided into more accurate assumptions of active site requirement in simulations under CLEERS.

Technical Accomplishments (SCR task): Hydrothermal Aging at >700˚C Leads to Catalyst Deactivation Due to Dealumination of SSZ-13

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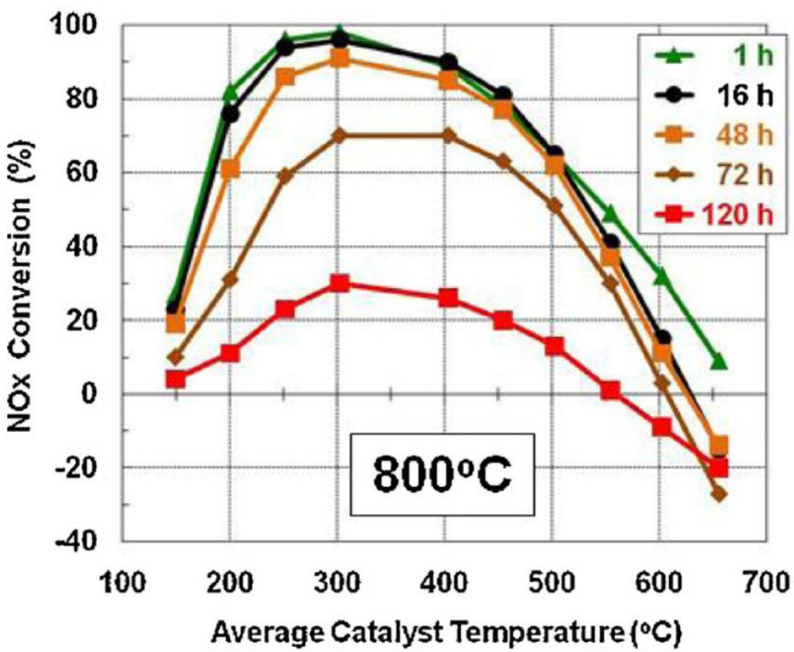
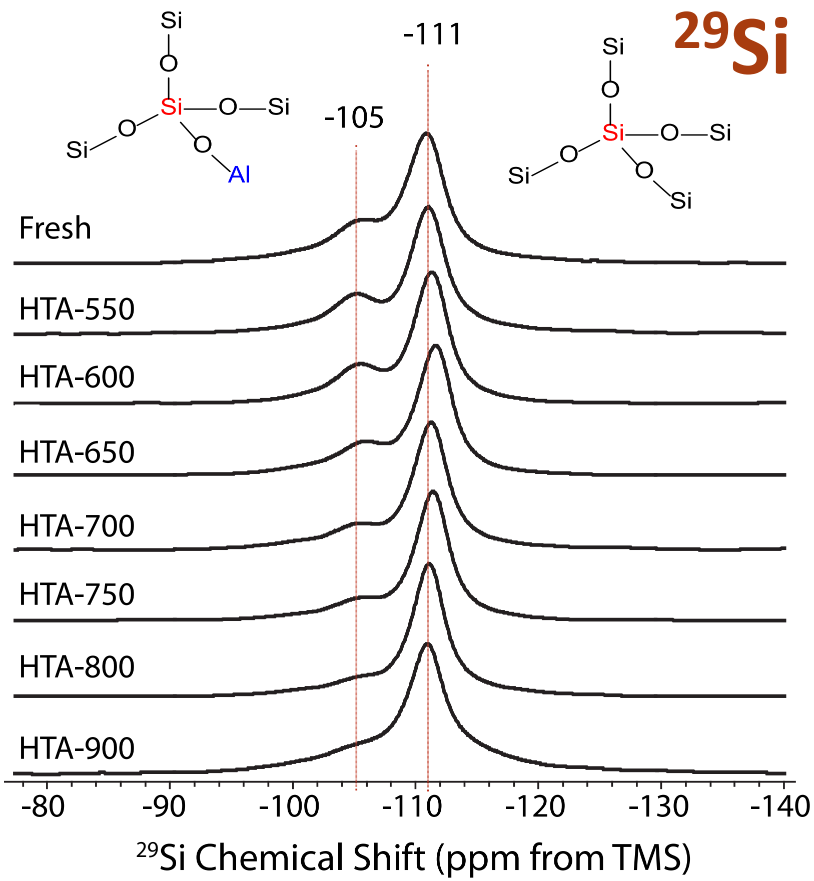
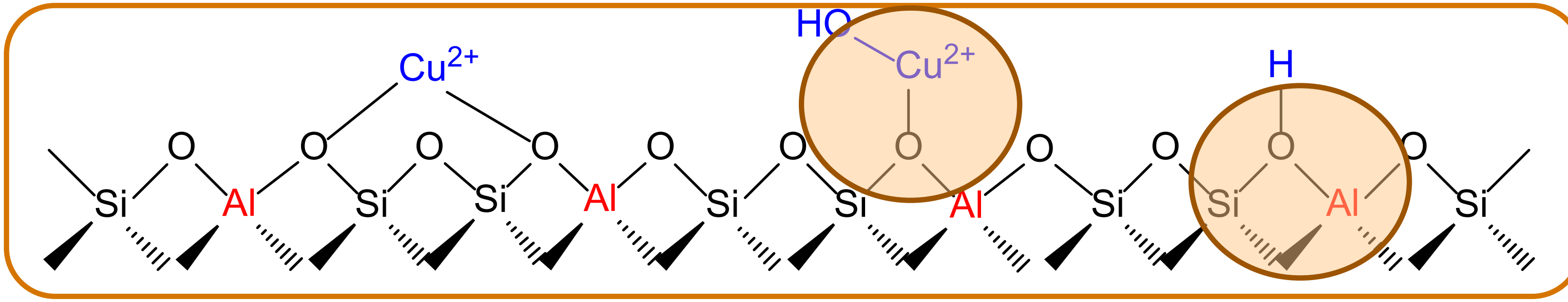


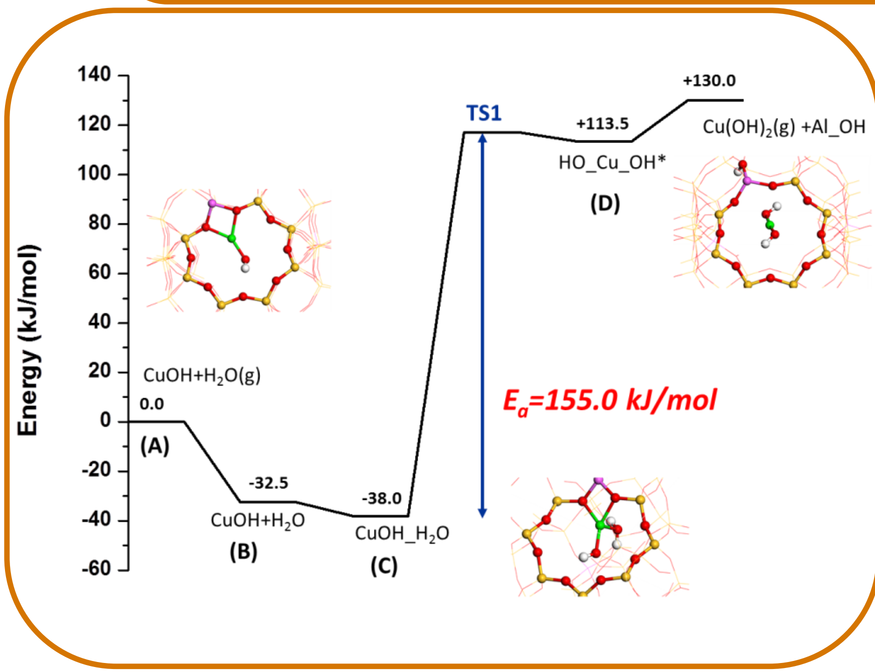


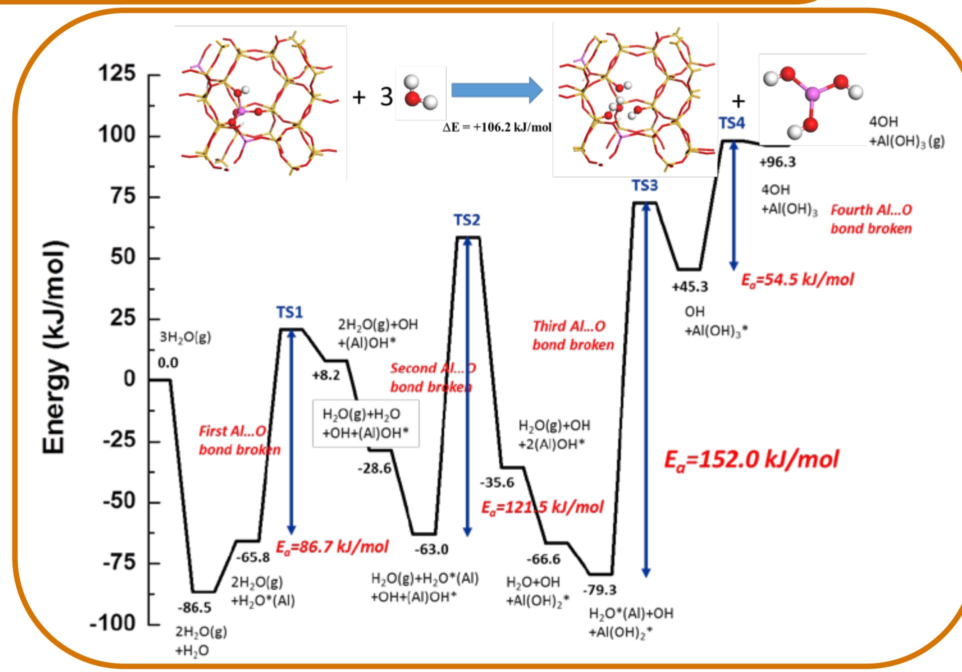
- Cu/SSZ-13 deactivates after thermal aging at 800˚C
- ^{27}Al and ^{29}Si NMR characterizations confirm that aging temperature of > 700ºC leads to dealumination of the zeolite support.

Cu/SSZ-13 (Si/Al = 12, Cu loading 2.1wt%)
HTA condition: 16 h at each target temperature in 10% H_2O/air (2 h at 900ºC).

Technical Accomplishments (SCR task):
DFT Confirmed the Stability of Two Cu-ion Sites

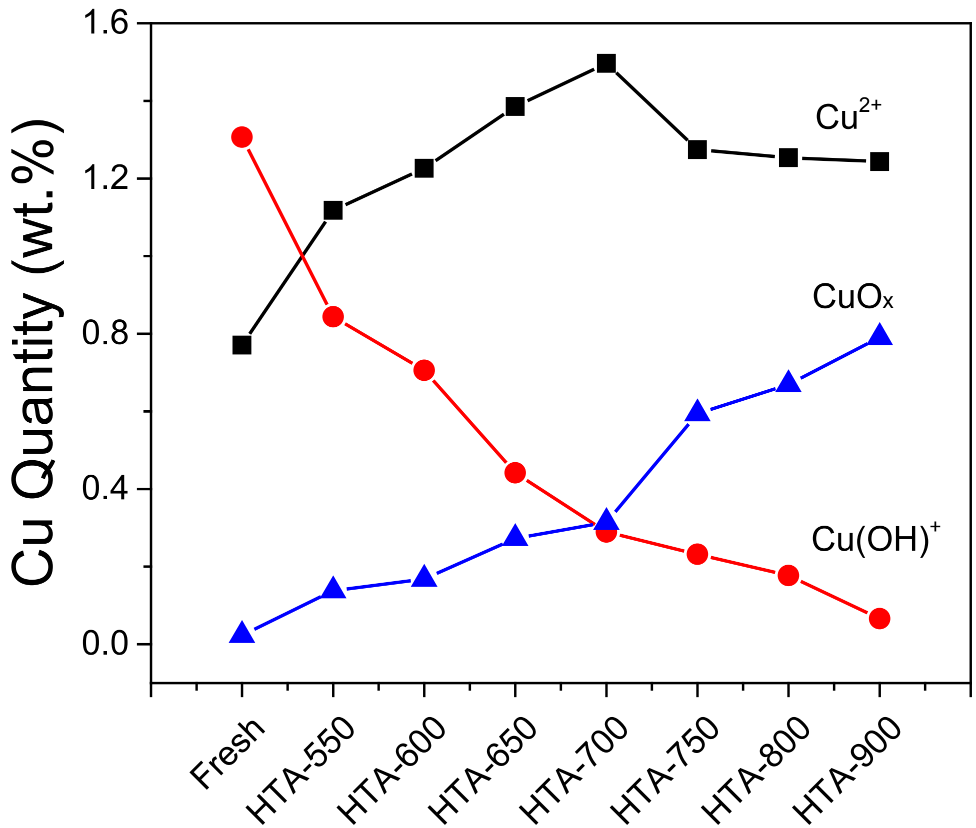


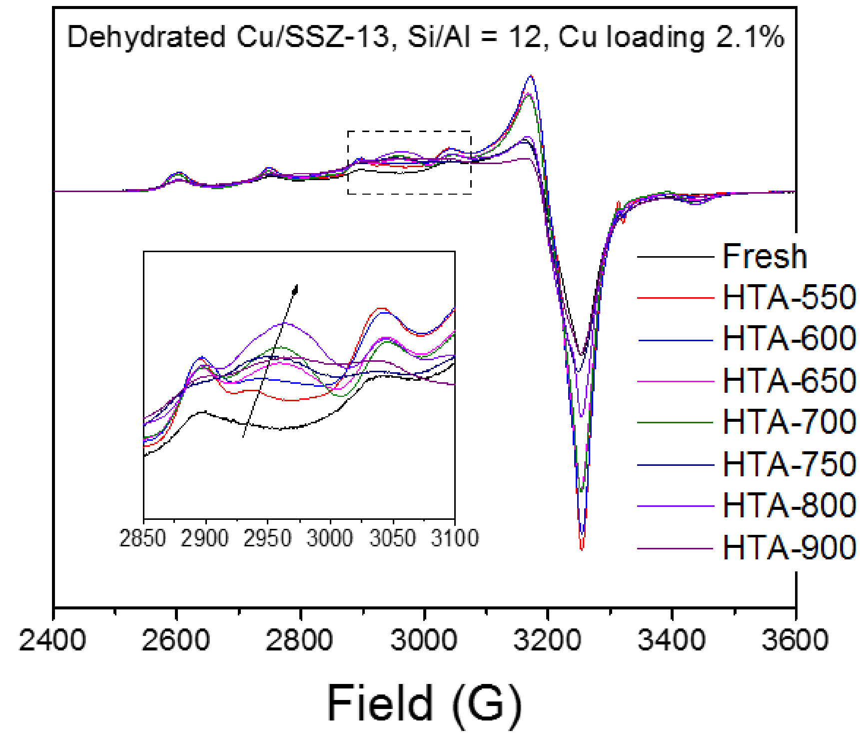




- Dealumination and CuOH removal require activation, which is achievable at high aging temperatures. Cu^{2+} removal is very hard.
- CuOx cluster formation from $Cu(OH)_2$ detachment followed by migration and agglomeration.

EPR Analysis Used to Understand Cu and Design More Active and Durable Catalysts





- Si/Al ratio of 10-20 and Cu/Al ratio of 0.2-0.3 are required for active, selective and durable Cu/SSZ-13 catalysts.

Technical Accomplishments (PNA task): Pd/Zeolites Are Promising Passive NO Adsorbers

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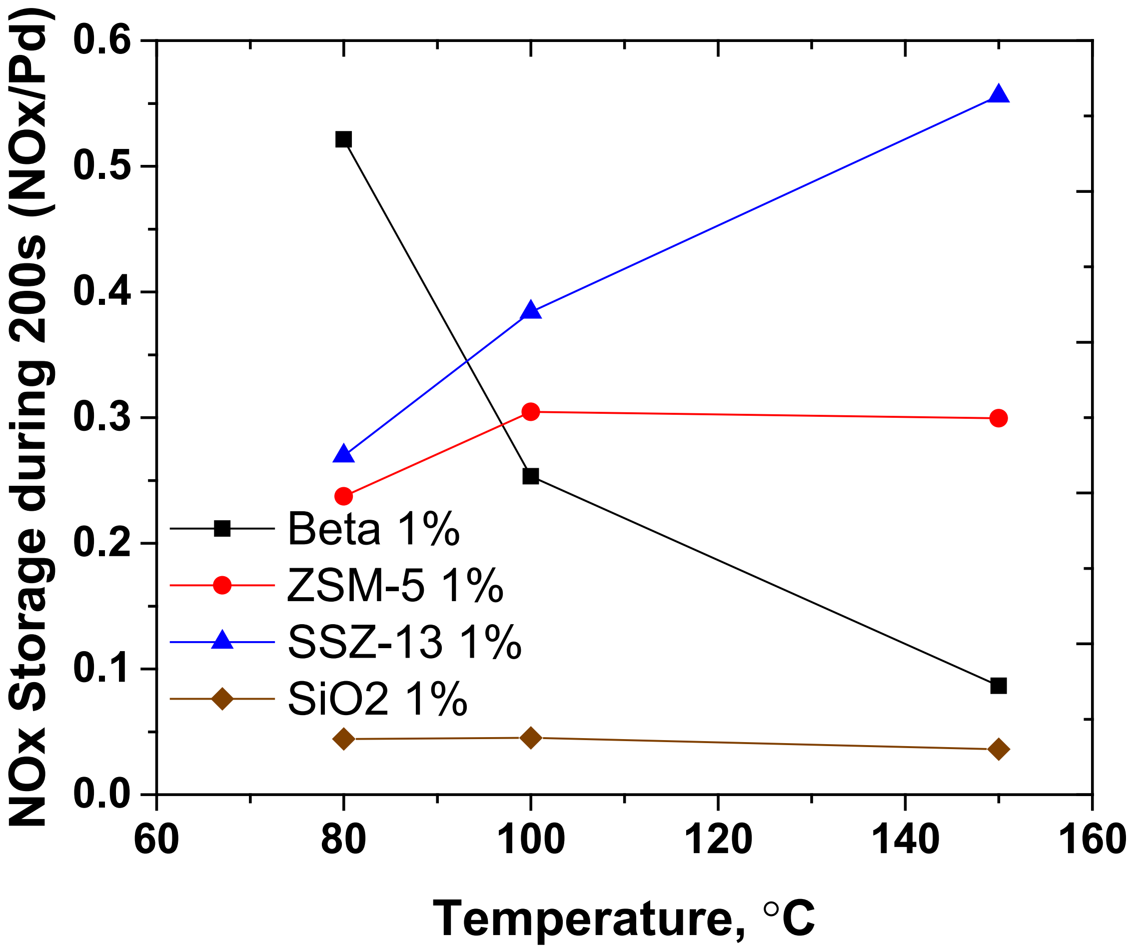

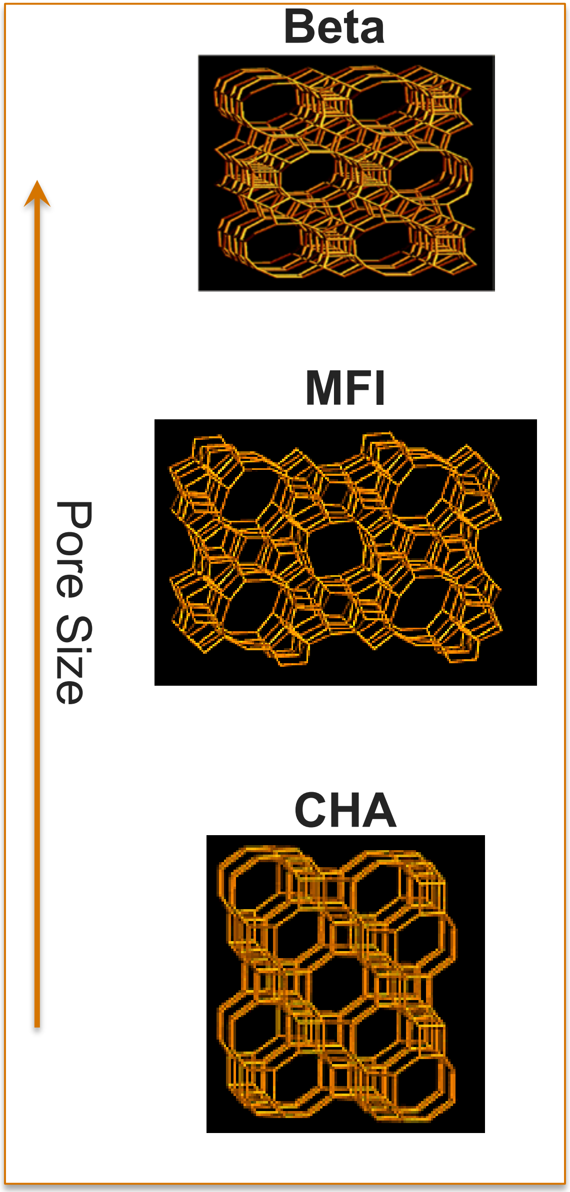

- Pd/Beta: the most efficient at T<100 °C and Pd/SSZ-13: the best at T>100 °C

Technical Accomplishments (PNA task):
NO Uptake Involves Surface Reaction with Pd

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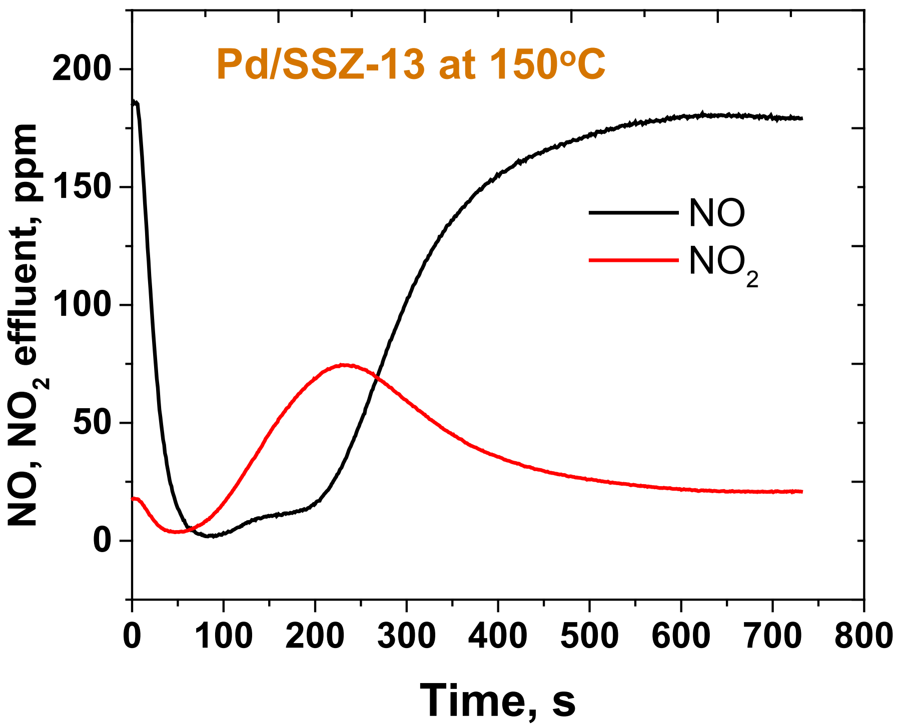
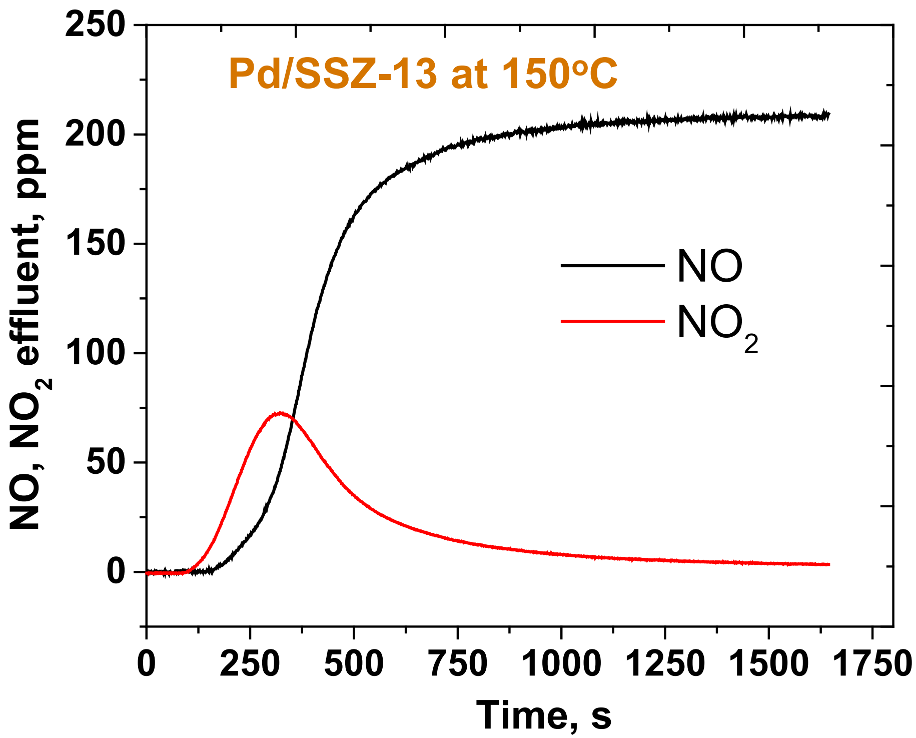
Standard Storage Test



Flow NO in the Absence of O_2



- NO storage is not a simple adsorption but involves surface reactions.

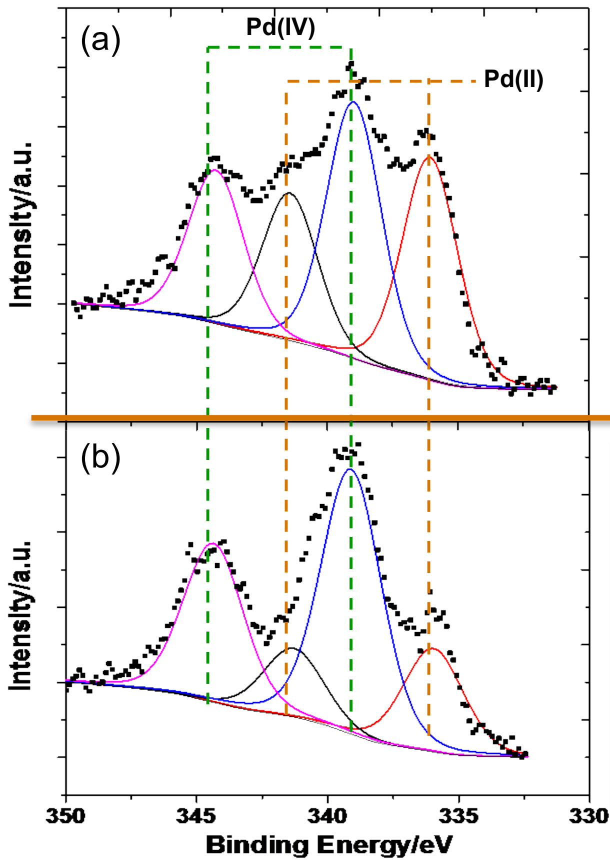
$$PdO_x + NO = PdO_{x-1} + NO_2$$
$$PdO_x + CO = PdO_{x-1} + CO_2$$

- Both reactions lower Pd oxidation state and facilitate NOx trapping.
- Same trends are observed for Pd/Beta and Pd/MFI catalysts as well.

Technical Accomplishments (PNA task):
in situ XPS Confirms Reduction of Pd(IV)

Oxidation (O_2; 500 °C)

Reduction (NO; 180 °C)

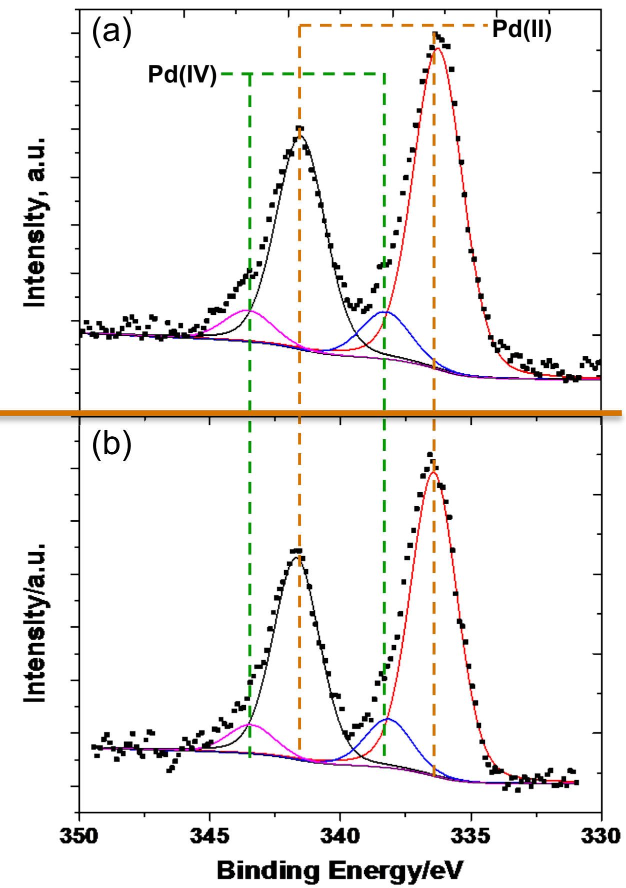


Pd/Beta (0.92 %)

	Oxidation	Reduction
Pd(II)	46.4%	87.1
Pd(IV)	53.6	12.9

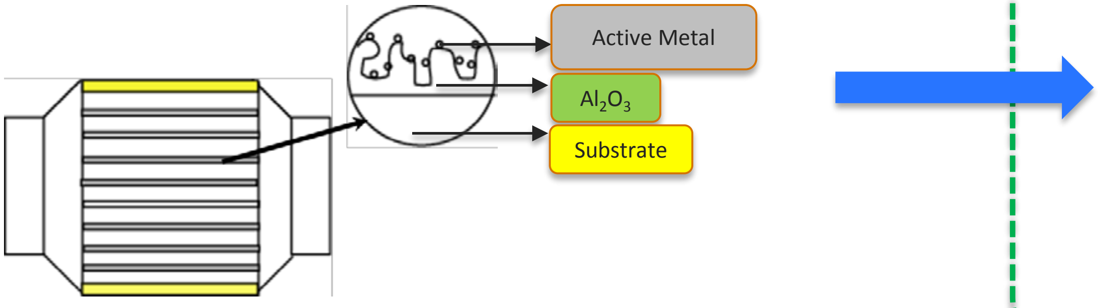
Pd/SSZ-13 (0.88 %)

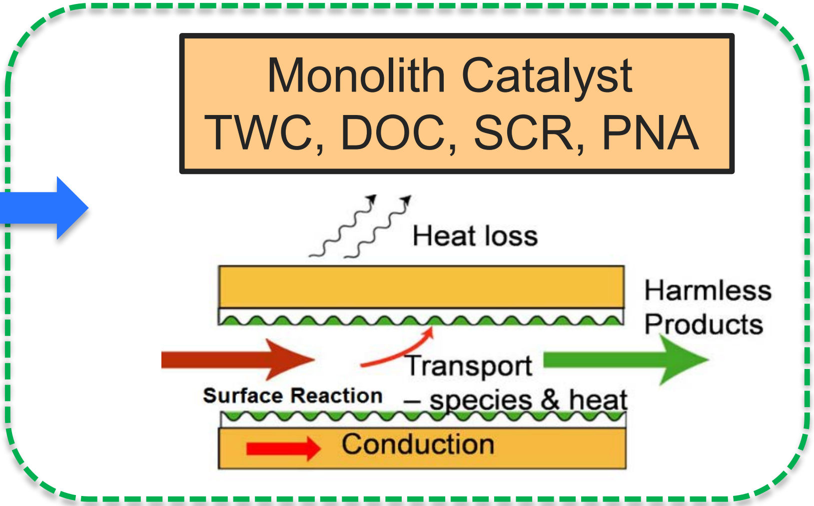
	Oxidation	Reduction
Pd(II)	27.4	86.1
Pd(IV)	75.6	13.9



- NO can effectively reduce Pd(IV) to Pd(II) at temperatures relevant to PNAs. (Can explain the formation of NO_2 during NO adsorption.)

Efficient Use of Parallel Computing Allows Up to 10x Faster Kinetics Simulations





- Framework developed under CLEERS project
- Generalized 1D catalyst model to simulate TWC, DOC, SCR or PNA
  - Governing equations for physics identical
  - Models differ in inherent surface chemistry
    - Capable of incorporating global or micro-kinetics
- Catalyst model parallelized to allow efficient use of clusters
  - Computing time *reduced by 10x* for new kinetics development

Technical Accomplishments (SCR task): Validated Comprehensive Kinetic Model over 6 Aging Conditions

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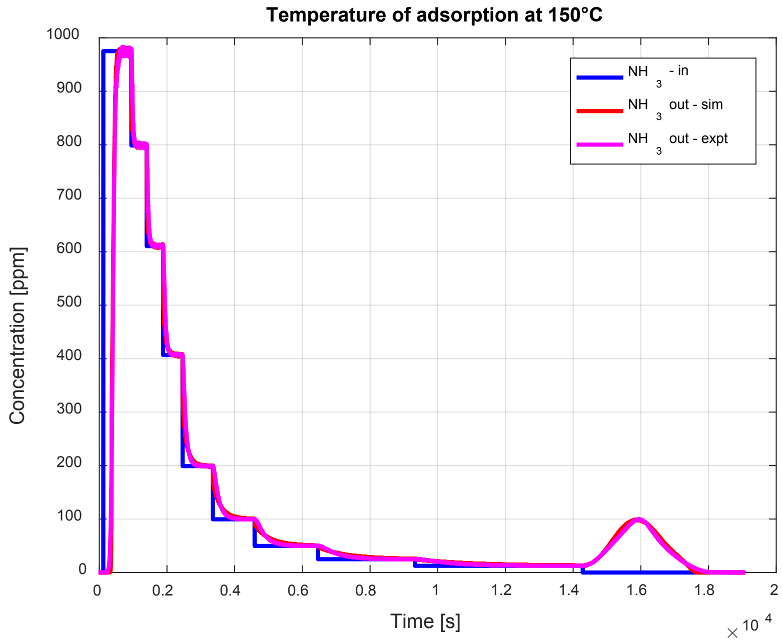


- NH_3 storage and kinetic data collected by ORNL using CLEERS SCR protocol over a range of aged states
- 2 site Tempkin mechanism
  - Cu^{2+} and Cu-OH dimer

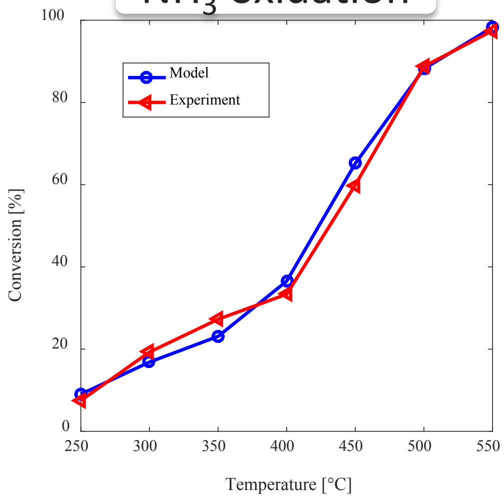
$$Cu - OH \xrightarrow{Aging} Cu_xO_y$$

  - On Cu_xO_y (increases with aging)

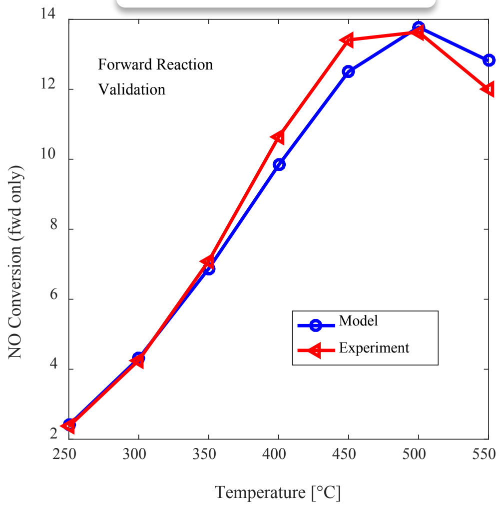
$$NH_3 + 1.25O_2 \xrightarrow{CuxOy} NO + 1.5H_2O$$

  - NO oxidation only on Cu-OH
  - NH_4NO_3 formation on Cu^{2+}

NH_3 oxidation

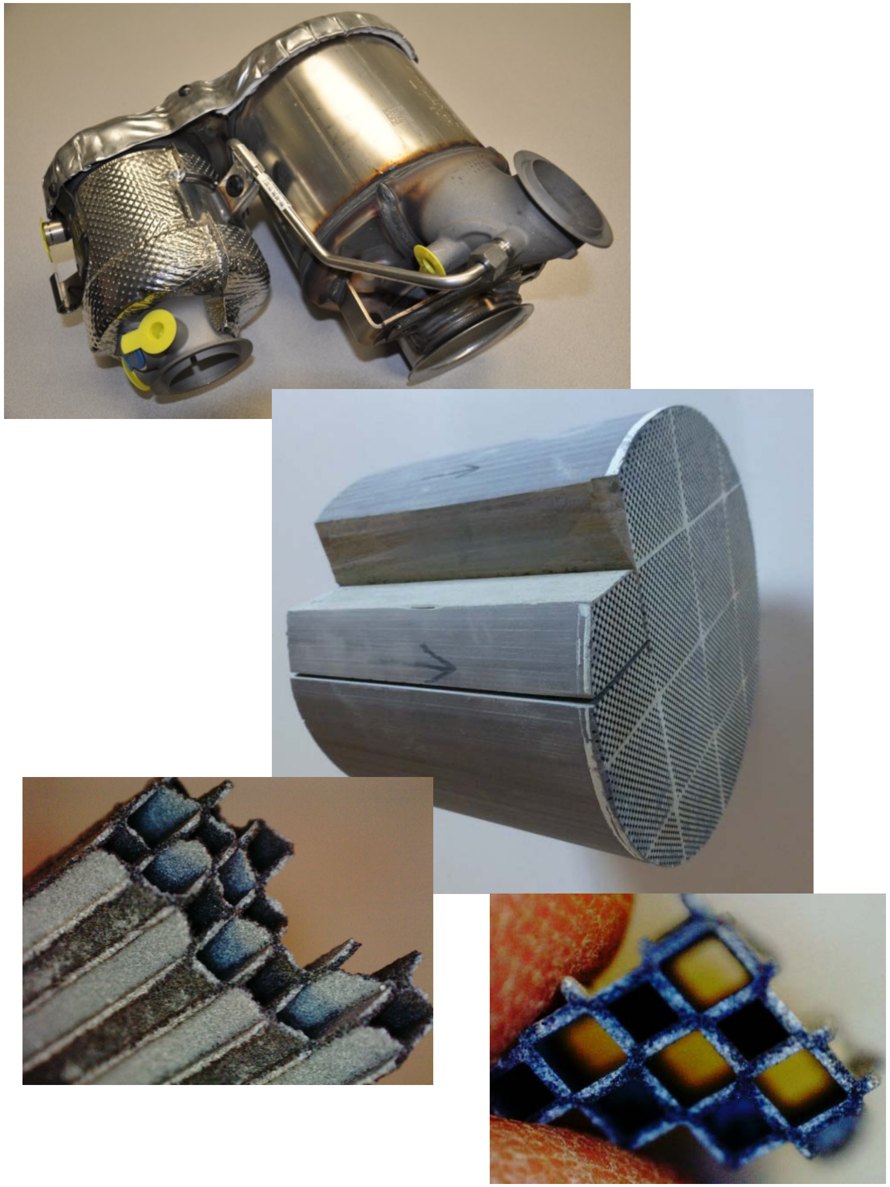


NO oxidation



Comprehensive kinetic model
Validated over 6 aging conditions

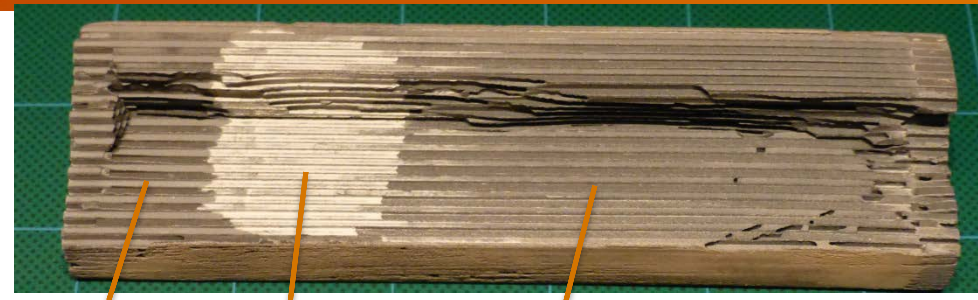
Technical Accomplishments (Particulate/filtration task):
Examination of Commercial SCR-filter



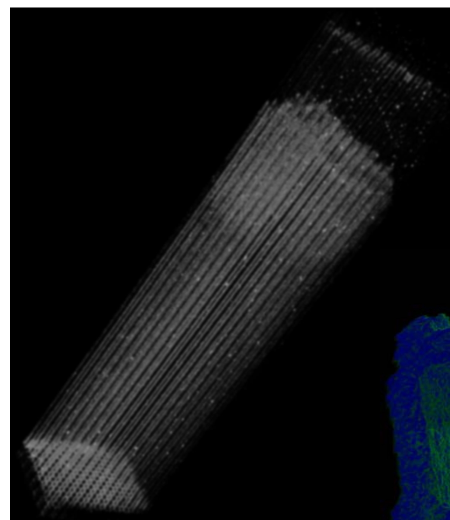
- SCR filter deployed on 2015 2-liter VW TDI cars was obtained from an auto parts dealer
- Although deployment of this specific system was cut short in the US by the VW emissions scandal, interest in SCR-filter technology and multi-functional filters remains strong
- Sophisticated, high-fidelity models will require detailed information on catalyst placement, wall permeability
- Coated filter was removed, sectioned, and examined visually and by X-Ray CT, SEM
- When it became apparent that catalyst distribution was complex, PNNL teamed with Justin Kamp (MIT, Kymanetics) for multi-resolution CT scans

Catalyst Coating Varies among Different Regions

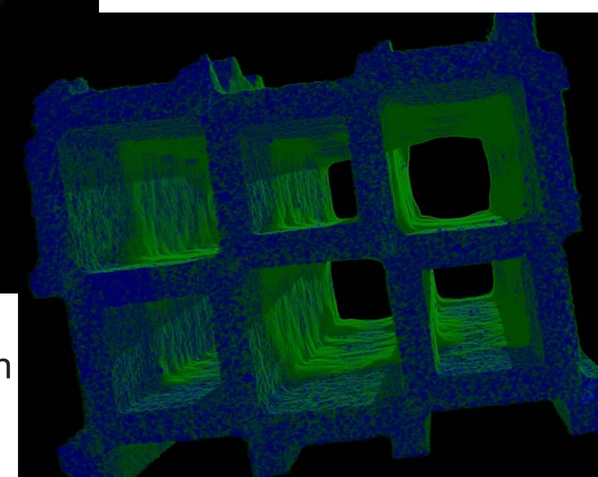
- At least three distinct regions were observed:
  - Region 1
    - Inlet end
    - ~ 15% or less of effective length
    - Relatively lightly coated, heavier on upstream side
  - Region 2
    - Near inlet end
    - ~ 20% or less of effective length
    - Heavily coated with surface deposits visible on both sides
    - Some empty pores in middle of wall
  - Region 3
    - Outlet end
    - ~ 70% of the effective length
    - Intermediate loading, heavier on downstream side
- Regions will likely have different permeability, filtration behavior, and chemical activity



Region 1 Region 2 Region 3



Catalyst density shown in CT scan of full segment, 47 μm resolution



Transition from Region 1 to Region 2, 3.6 μm resolution, catalyst shown in green

X-ray CT by Justin Kamp (MIT, Kymanetics, Inc.)

Technical Accomplishments (LTAT task): Finalized the Low Temperature Storage Catalyst Test Protocol

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- Finalized the Low Temperature Storage Catalyst Test Protocol
  - Currently under review by the APTLC
- Nearing completion of the Three-Way Catalyst Test Protocol
- Supporting update of the June 2013 ACEC Roadmap
  - Targeting June 2017 completion

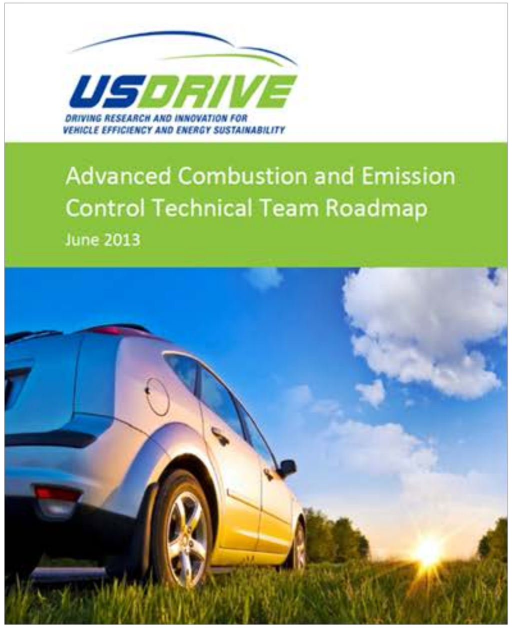
- Continue Interaction
  - Bi-monthly ACEC participation in person
  - Bi-weekly LTAT participation via teleconference
- Work with ACEC to identify LTAT Group focus beyond protocol development
  - E.g., Modeling needs and priority identification


Aftertreatment Protocols for Catalyst Characterization and Performance Evaluation:
Low-Temperature Storage Catalyst Test Protocol

The Advanced Combustion and Emission Control (ACEC) Technical Team
Low-Temperature Aftertreatment Group

June 2016

USDRIVE
DRIVING RESEARCH AND INNOVATION FOR VEHICLE EFFICIENCY AND ENERGY SUSTAINABILITY



Response to Previous Year Reviewers' Comments

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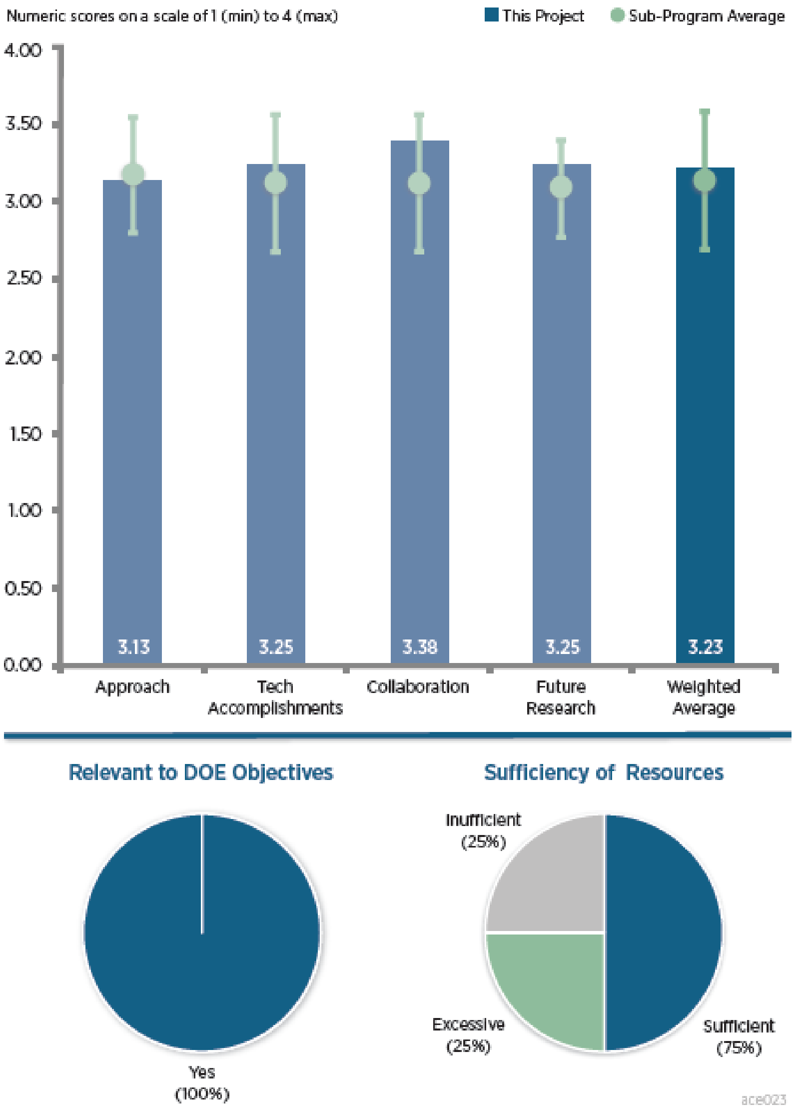
- Nearly all the comments from the reviewers last year were very supportive and complimentary.
- Some comments/recommendations included:
  1. ..contemporary direction is on Cu zeolites, not Fe zeolites...
  2. ..SCR should address deactivation mechanisms at an earlier stage...
  3. ..accelerate efforts on PNA development...
- PNNL response:
  1. SCR effort focuses on both low temperature mechanisms and high temperature hydrothermal stability of Cu/SSZ-13 (slides 6-10).
  2. Elucidate the deactivation mechanisms of Cu/SSZ-13 under hydrothermal aging (slides 8-10).
  3. PNA on Pd/zeolite is the major focus (slides 11-13).



Collaboration and Coordination with Other Institutions

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Collaborators/Coordination

- DOE Advanced Engine Crosscut Team (this group is the primary sponsor and overseer of all activities)
- CLEERS Focus Groups
- USCAR/USDRIVE ACEC team
- 21CTP partners
- Oak Ridge National Lab
- Kymanetics, Inc.
- Very active collaboration with an NSF/DOE-funded program with partners at Purdue, Notre Dame, WSU, Cummins and ANL

Acknowledgements

- <u>PNNL</u>: Haiying Chen (Johnson Matthey), Laura Righini (Politechnico Milano), John Luo (Cummins), Alla Zelenyuk, Carl Justin Kamp (MIT, Kymanetics)
- <u>ORNL</u>: Stuart Daw, Jim Parks, Josh Pihl, John Storey, Vitaly Prikhodko, Samuel Lewis, Mary Eibl, and support from the ORNL team
- <u>DOE Vehicle Technologies Program</u>: Gurpreet Singh and Ken Howden

Remaining Challenges and Barriers

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SCR

- Understand the nature and location of the active Cu species in Cu-CHA SCR catalysts during operation.
- Elucidate the exceptional stability of SSZ zeolites.
- Advance the level of understanding of the fast-SCR reaction, mechanism, requirements and barriers.

LTAT

- Low temperature oxidation of short-chain HCs including methane.

PNA

- Further understand the role of the zeolite framework in determining the NOx storage properties of Pd sites.
- Understand Pd movement under oxidizing and reducing reaction conditions.
- Identify the roles of Pd ions in different oxidation states in eth NOx storage/release processes.

Particulate/Filtration

- Detailed performance models are needed for production GPF and multi-functional exhaust filters, which are starting to enter the marketplace
- Ash accumulation in GPF walls can help with initial soot capture efficiency, but could raise long-term performance issues

Future Work

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SCR

- In operando EPR studies on SCR over Cu/CHA: quantification of Cu(II) and Cu(I) under all reaction conditions with PNNL model catalysts.
- New zeolite supports: LTA, SSZ-16, 17 and 39.
- Co-catalysts for SCR: binary catalyst system(s) for superior NO activation.

PNA

- In situ synchrotron based studies on PNA catalysts.
- Hydrothermal aging effects for the PNA catalysts.
- Sulfur and HC tolerance for the PNA catalysts.

Particulate/Filtration

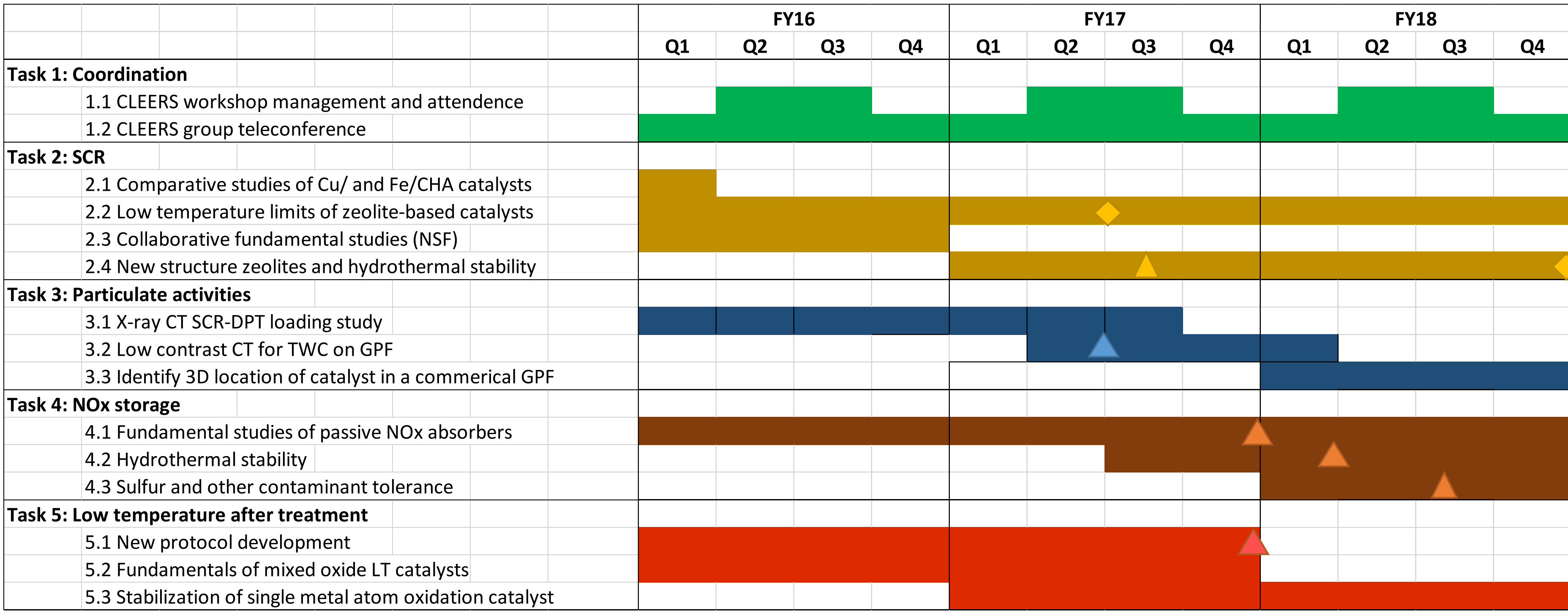
- Obtain sub-micron CT data showing detail of catalyst/wall interactions in commercial SCR-filter.
- Develop tools to identify 3D location of catalysts in chemically similar filter substrate walls.

LTAT

- Continue addressing the issues for practical applications of promising emerging catalysts, including HCs and S effects.
- Work with ACEC to identify LTAT Group focus beyond protocol development, e.g., modeling needs and priority identification.

Any proposed future work is subject to change based on funding levels.

Proposed Schedule for PNNL CLEERS Activities Shifts Focus to PNA for Low T Applications



▲ Milestones
◆ Go/No-Go Decision

Any proposed future work is subject to change based on funding levels.

Summary

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SCR

- Determined Low-temperature SCR mechanism via kinetics, spectroscopic and density functional theory studies for Cu/SSZ-13.
- Provided atomic level understanding on the transformation of Cu active centers in Cu/SSZ-13 during hydrothermal aging.

LTAT

- Finalized the low temperature storage catalyst test protocol, and nearing completion of 3-way catalyst test protocol.

PNA

- Confirmed NOx storage/release properties of Pd loaded zeolites (CHA, MFI, Beta).
- Determined that both NO and CO are able to reduce Pd(IV) to Pd(II) or lower oxidation states.
- Identified the origin of NO_2 formation during NO uptake in Pd-zeolites.
- Provided clear evidence for the migration of active phase out of and into the zeolite framework under reducing and oxidizing conditions, respectively.

Particulate/Filtration

- Characterized catalyst location in three distinct coating regimes along the axial length of a commercial SCR-filter.

Technical Back-Up Slides

Why Is A High Cu Loading More Detrimental Than Beneficial?

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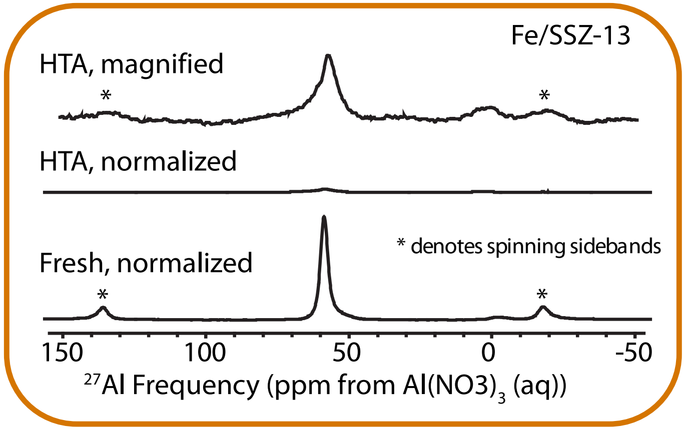

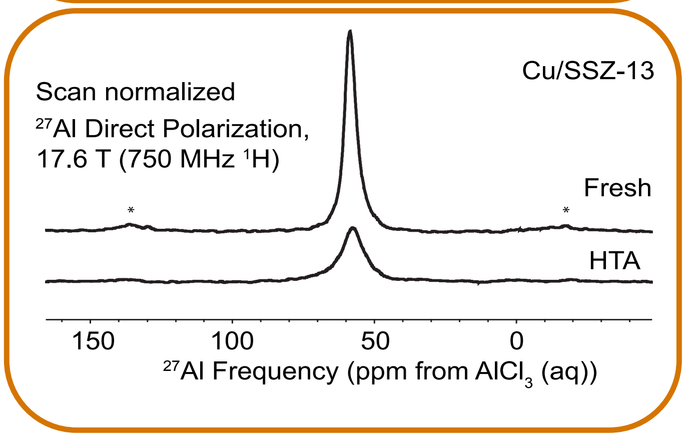

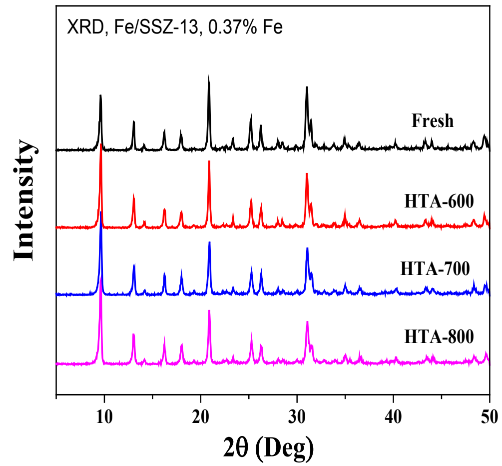

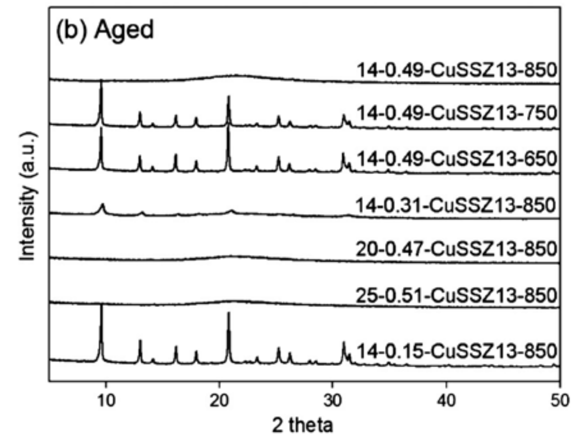

Kim, et al. Journal of Catalysis 311 (2014) 447–457

- Dealumination does not necessarily cause CHA structure damage.
- Mobile CuOx clusters larger than CHA pore opening induce structure damage.
- Si/Al ratio of 10-20 and Cu/Al ratio of **0.2-0.3** are required for active, selective and durable Cu/SSZ-13 catalysts.

HTA Affects SCR Activities of Cu/SSZ-13 at Both Low and High Temperatures

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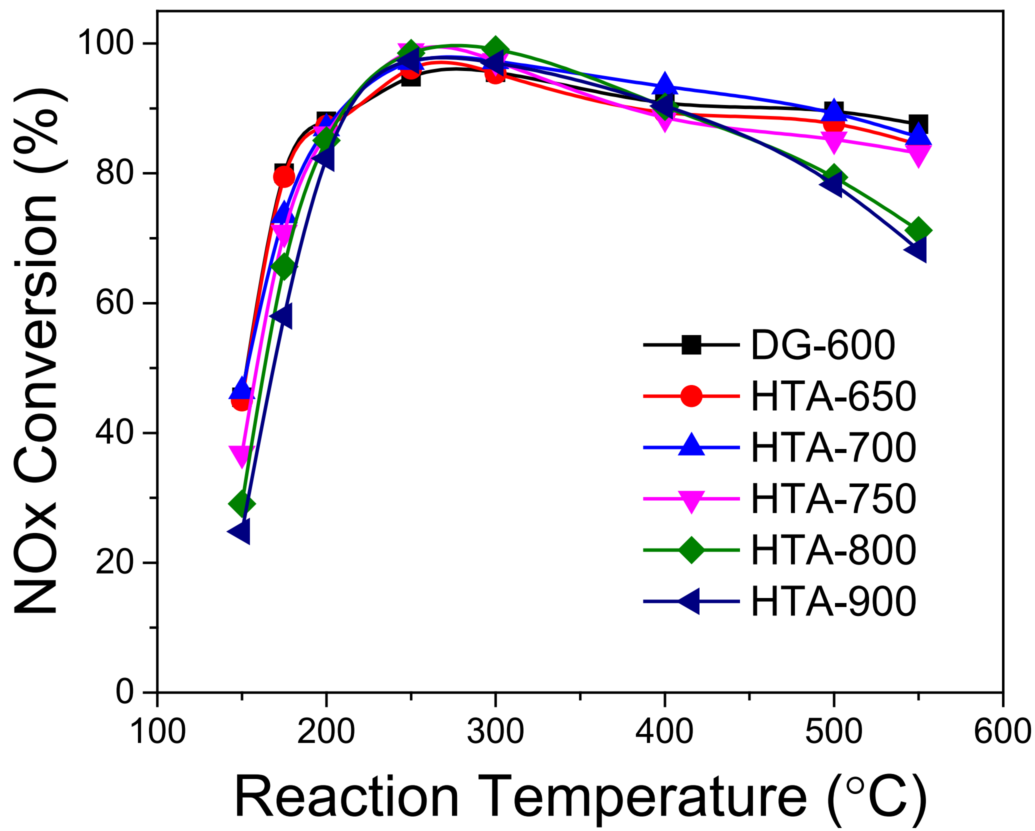
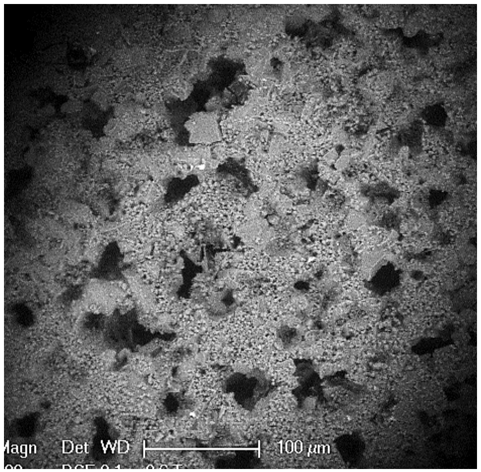
Institute for INTEGRATED CATALYSIS

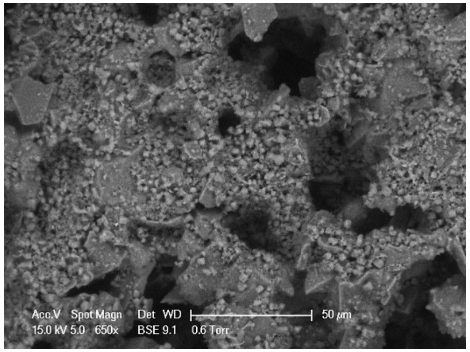
Standard SCR: $4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O$

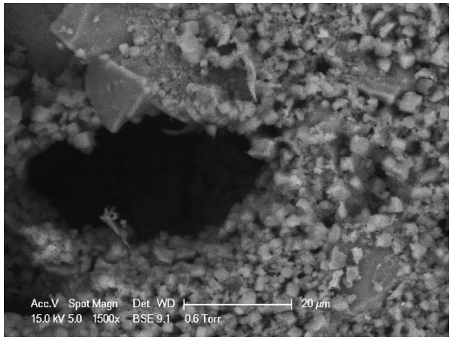


- GHSV = 100k h^{-1} in powder form, corresponding to ~25k h^{-1} in washcoated form.
- The effects of HTA(hydrothermal aging) (>700°C) on catalyst performances are apparent at <200 and >400 °C.

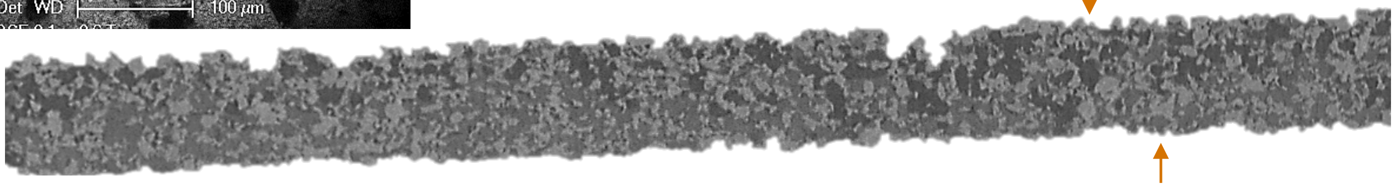
Electron Microscopy of SCR-Filter Wall





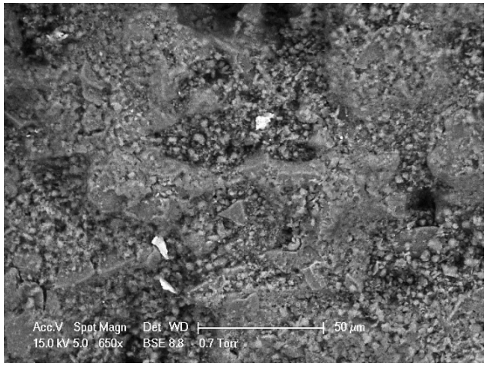


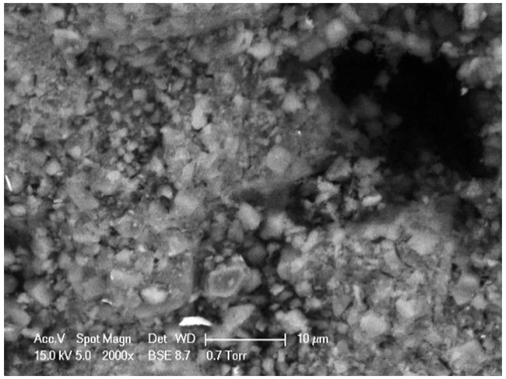
Inlet



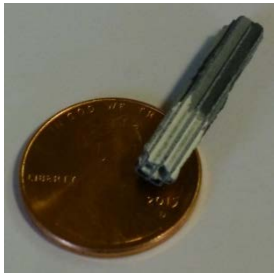
Region 3 (Kymanetics)

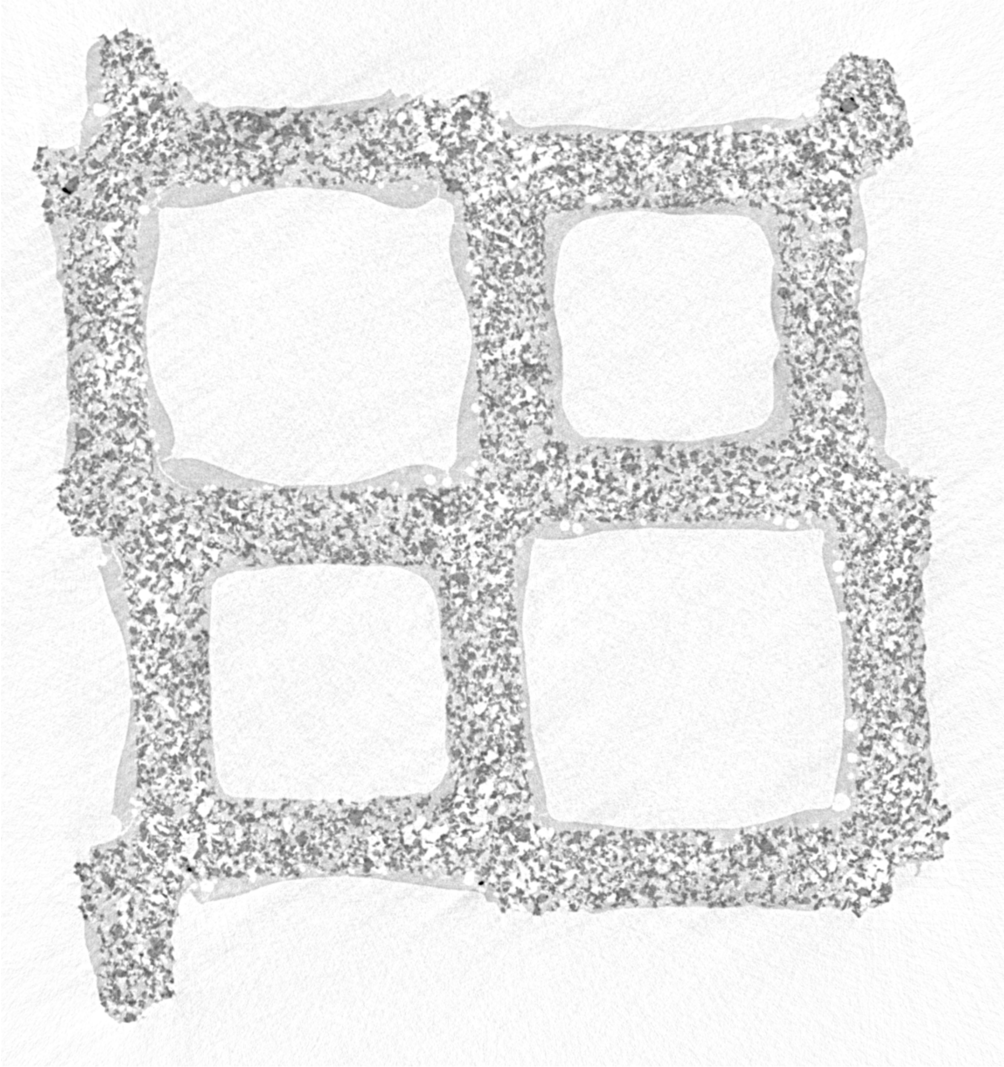
Outlet





X-ray CT of Thick Coating (Region 2) in SCR - Filter





- 1.7 μm resolution
- Coating covers most surface pores
- Empty pores inside the filter wall under the coating in some locations
- Some internal pores filled